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Patentanmeldung Nr.   Patent application No.   Demande de brevet n°

02292851.9

Der Präsident des Europäischen Patentamts;
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
p.o.

R C van Dijk

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Anmeldung Nr: Anmeldetag:
Application no.: 02292851.9 Date of filing: 15.11.02
Demande no: Date de dépôt:

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Bezeichnung der Erfindung/Title of the invention/Titre de l'invention:
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New perovskite catalyst for the partial oxidation of natural gas

In Anspruch genommene Priorität(en) / Priority(ies) claimed /Priorité(s)
revendiquée(s)
Staat/Tag/Aktenzeichen/State/Date/File no./Pays/Date/Numéro de dépôt:

Internationale Patentklassifikation/International Patent Classification/
Classification internationale des brevets:

C01B/

Am Anmeldetag benannte Vertragstaaten/Contracting states designated at date of
filing/Etats contractants désignées lors du dépôt:

AT BE BG CH CY CZ DE DK EE ES FI FR GB GR IE IT LI LU MC NL PT SE SK TR

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The present invention relates to a new catalysts for the partial oxidation of hydrocarbons.

The catalytic partial oxidation of hydrocarbons, natural gas or methane to synthesis gas, which consist in mixtures of hydrogen (H_2) and carbon monoxide (CO) in various proportions, has been processed for many years. While currently limited as an industrial process, the partial oxidation is also of interest for the significant released heat and for the use of smaller reactors. More particularly, the partial oxidation of methane at short residence time is a goal to reach synthesis gas using an alternative process to the steam reforming process, which is today the most popular one.

Synthesis gas can be used as feed for fuel cell or as a reducing atmosphere in the metallurgic industry but it is mainly the key step for activation of methane for the indirect production of methanol and middle distillate in the petrochemical and chemical industries.

The advantage of the catalytic partial oxidation of methane is mainly its strong exothermic character in the short residence time. Both parameters allow producing synthesis gas with lower investment cost without delivering large quantities of external energy.

Nevertheless, because this strong exothermic character of the total oxidation reactions, the temperature of the catalytic bed reaches more than well above 1000°C.

There is thus a need for very stable catalyst in terms of metal sintering and support resistance.

Furthermore, as the catalyst activity affects the thermal profile of the reactor, a careful modulation is therefore required to avoid hot spot in the reactor which can light on the homogeneous reaction.

A novel approach relates to the possibility of introducing the metal in the crystallographic structure of a given material and then to activate the catalyst by reducing the metal "*in situ*" or under hydrogen flow. This allows in some case to develop a strong interaction between metal and surface. Some of these catalysts have a Perovskite structure.

US 5,149,516 discloses the partial oxidation of methane to produce carbon monoxide and hydrogen using a Perovskite catalyst, such as $LaCoO_3$.

US 5,447,705 discloses a catalyst for the partial oxidation of methane or of a gaseous mixture containing methane, said catalyst preferably having a Perovskite structure with LaFeNi as a cation composition. However, in the reported examples it is very difficult

to balance the structure stability. On one hand, if the reducible metal (Ni and Co) is present in large amount, the structure is completely reduced and the Perovskite structure becomes unstable. On the other hand, if the reducible cation is present in low amount, the catalytic activity is poor and does not allow to work with short residence time.

US 6,110,861 discloses a two-part catalyst comprising a dehydrogenation portion and an oxide-ion conducting portion.

WO 0160742 discloses a catalysts and a processes for the catalytic conversion of hydrocarbons to carbon monoxide and hydrogen employing new families of chromium-rare earth based catalysts .

Today, none of the existing catalytic partial oxidation processes is able to provide a sufficiently high conversion of the reactant gas together with a high selectivity of CO and H_2 reaction products, without using high quantities of rare and costly catalysts, nor without experiencing adverse effects such as an excessive coking of the catalyst, or a premature catalyst failure by its lack of heat resistance or by its mechanical instability or even by the mechanical instability of its structure.

That is why there is a continuing need for new catalysts that are mechanically stable and retains a high level of activity and selectivity to CO and H_2 products under conditions of high temperature, without excessive coking.

The inventors have found that the catalysts of the present invention overcome some of these drawbacks.

Accordingly, the present invention provides a composition characterized in that it essentially consists in a solid solution of a mixture of at least a perovskite cristallographic structure with nickel and/or rhodium metal.

The composition as defined above is more particularly represented by the general formula (I) :

$$[A_zA'_{1-z}][B_{1-x-y}Ni_xRh_y]O_{3-\delta} \qquad (I)$$

wherein :

A and A' are different and are selected from the Lanthanide or the Actinide families or from the group II_a of the Mendeleev's periodical table of elements;

B is selected from the transition metal groups of columns IIIb, IVb, Vb, VIb, VIIb, Ib and IIb and group VIIIb of the Mendeleev's periodical table of elements;

$0 < x \leq 0.7$,

$0 \leq y \leq 0.5$,

$0 \leq x+y \leq 0.8$,

$0 \leq z \leq 1$ and

δ is the sub stœchiometric value of oxygen to obtain the electric neutrality of the Perovskite compound.

According to one particular aspect the invention A and A' are independently chosen from La, Ce, Ca or Sr. A is preferably La.
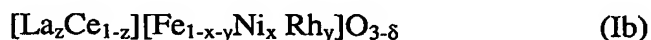
According to another particular aspect of the invention, B is chosen from Mn, Fe, Co or Al.

The invention is more particularly relates a composition, characterized in that it is represented by the formula (Ia):

$$[La_zA'_{1-z}][Fe_{1-x-y}Ni_x Rh_y]O_{3-\delta} \qquad (Ia)$$

wherein A', x, y, and z and δ are as hereinabove defined for the formula (I).

Among the compounds represented by the formula (Ia), those represented by the formula (Ib) :

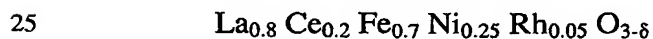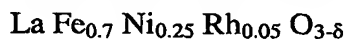$$[La_zCe_{1-z}][Fe_{1-x-y}Ni_x Rh_y]O_{3-\delta} \qquad (Ib)$$

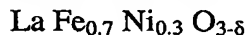wherein x, y, and z and δ are as hereinabove defined for the formula (I),
are preferred.

According to a preferred aspect of the invention, in the formulas (I) (Ia) or (Ib), $0 < x \leq 0.5$.

According to another preferred aspect of the invention, in the formulas (I) (Ia) or (Ib), $0 < y \leq 0.25$ and $z < 1$.

The invention more spefically consists in the following compositions :

La $Fe_{0.7}$ $Ni_{0.25}$ $Rh_{0.05}$ $O_{3-\delta}$

$La_{0.8}$ $Ce_{0.2}$ $Fe_{0.7}$ $Ni_{0.25}$ $Rh_{0.05}$ $O_{3-\delta}$

$La_{0.8}$ $Ce_{0.2}$ $Fe_{0.7}$ $Ni_{0.3}$ $O_{3-\delta}$

While two composition have been selected for comparison

La $Fe_{0.7}$ $Ni_{0.3}$ $O_{3-\delta}$

La $Fe_{0.95}$ $Rh_{0.05}$ $O_{3-\delta}$

According to another aspect of the present invention, the composition as defined as herein above, is used as a catalyst of the partial oxydation of natural gas and/or light hydrocarbons to synthesis gas, as a catalyst of the steam and/or dry reforming of natural gas

and/or light hydrocarbons (C_2-C_4) to synthesis gas and/or selective oxidations.

By light hydrocarbons, those which have a carbon chain containing from two to four carbon atoms (C_2-C_4), are more sepecifically within the scope of the present invention.

The composition of the invention are more specifically worked on in the operating catalyst temperature conditions in the range of 500 to 1300°C and preferably between 600 to 1100°C, and/or in the operating catalyst pressure conditions in the range of 10^5 Pa to 3 10^6 Pa and preferably between 10^5 Pa to 10^6 Pa.

In the use herein before mentioned uses, the oxydant gaseous feed is of any kind; it is preferably pure oxygen, oxygen and inert gas mixture, steam, carbon dioxide or a mixture of part or/and all of them.

According to another aspect the present invention, the composition as defined as herein above, is used as a catalyst of hydrogenation reactions or as a catalyst of dehydrogenated oxydative reactions.

The following examples illustrate the present invention without limiting it.

Example 1: LaFe$_{0.7}$Ni$_{0.25}$Rh$_{0.05}$O$_3$ (Invention)

5.3 g of La(NO$_3$)$_3$, 4.6 g of Fe(NO$_3$)$_3$, 1.2 g of Ni(NO$_3$)$_2$ and 0.83 g of Rh nitrate solution 10 % w/w are dissolved in 300 ml of distilled water and slowly dropped in a solution containing 7.7 g of citric acid dissolved in 400 ml of ethylene glycol. After mixing, the resulting solution are heated at 90°C for 4 h. The evaporation of water from the solution brings to the formation of a sol (colloidal solution with micrometric micelles). The catalyst is dried in oven at 90°C then the oven temperature is increased to 180°C over night. In this step, a gel is formed and dried. The obtained solid is calcined at 500°C for 4 h and then at 900°C for 12 h. The XRD shows the perovskite cubic pattern (figure 1) and the surface area after calcination is 8 m^2/g. Figure 1 discloses XRD patterns of LaFe$_{1-x}$M$_x$O$_3$ catalysts after calcination at 900°C (M$_x$ = Ni$_{0.3}$, Ni$_{0.25}$Rh$_{0.05}$ or Rh$_{0.05}$). (O) LaFeMO$_3$ perovskite structure.

Example 2: La$_{0.8}$Ce$_{0.2}$Fe$_{0.7}$Ni$_{0.25}$Rh$_{0.05}$O$_3$ (Invention)

5.3 g of La(NO$_3$)$_3$, 1.8 g Ce(NO$_3$)$_3$, 5.7 g of Fe(NO$_3$)$_3$, 1.5 g of Ni(NO$_3$)$_2$ and 1.0 g of Rh nitrate solution 10 % w/w are dissolved in 400 ml of distilled water and slowly dropped in a solution containing 9.5 g of citric acid dissolved in 500 ml of ethylene glycol. After

mixing, the resulting solution is heated at 90°C for 4 h. The evaporation of water from the solution brings to the formation of a sol (colloidal solution with micrometric micelles). The catalyst is dried in oven at 90°C then the oven temperature is increased to 180°C over night. In this step, a gel is formed and dried. The obtained solid is calcined at 500°C for 4 h and then at 900°C for 12 h. The XRD shows the perovskite cubic pattern and the reflection of the CeO_2 phase (Figure 2). The surface area after calcination is 10 m^2/g. Figure 2 discloses XRD patterns of $La_{0.8}Ce_{0.2}Fe_{0.7}Ni_{0.25}Rh_{0.05}O_3$ catalysts after calcination at 900°C / (+) ABO_3 perovskite structure, (*) CeO_2 compound.

Example 3: $LaFe_{0.7}Ni_{0.3}O_3$ (Comparative example)

5.3 g of $La(NO_3)_3$, 4.7 g of $Fe(NO_3)_3$, 1.4 g of $Ni(NO_3)_2$ are dissolved in 300 ml of distilled water and slowly dropped in a solution containing 7.7 g of citric acid dissolved in 400 ml of ethylene glycol. After mixing, the resulting solution is heated at 90°C for 4 h. The evaporation of water from the solution brings to the formation of a sol (colloidal solution with micrometric micelles). The catalyst is dried in oven at 90°C then the oven temperature is increased to 180°C over night. In this step, a gel is formed and dried. The obtained solid is calcined at 500°C for 4 h and then at 900°C for 12 h. The XRD shows the perovskite cubic pattern (Figure 1) and the surface area after calcination is 8 m^2/g.

Example 4: $LaFe_{0.95}Rh_{0.05}O_3$ (Comparative example)

5.3 g of $La(NO_3)_3$, 6.3 g of $Fe(NO_3)_3$, and 0.84 g of Rh nitrate solution 10% w/w are dissolved in 300 ml of distilled water and slowly dropped in a solution containing 7.7 g of citric acid dissolved in 400 ml of ethylene glycol. After mixing, the resulting solution is heated at 90°C for 4 h. The evaporation of water from the solution brings to the formation of a sol (colloidal solution with micrometric micelles). The catalyst is dried in oven at 90°C then the oven temperature is increased to 180°C over night. In this step, a gel is and dried. The solid obtained is calcined at 500°C for 4 h and then at 900°C for 12 h. The XRD shows the perovskite cubic pattern (Figure 1) and the surface area after calcination is 5 m^2/g.

Example 5: $La_{0.8}Ce_{0.2}Fe_{0.7}Ni_{0.3}O_3$ (Invention)

4.3 g of $La(NO_3)_3$, 1.4 g $Ce(NO_3)_3$, 4.6 g of $Fe(NO_3)_3$, 1.4 g of $Ni(NO_3)_2$ are dissolved in

400 ml of distilled water and slowly dropped in a solution containing 9.5 g of citric acid dissolved in 500 ml of ethylene glycol. After mixing, the resulting solution is heated at 90°C for 4 h. The evaporation of water from the solution brings to the formation of a sol (colloidal solution with micrometric micelles). The catalyst is dried in oven at 90°C then the oven temperature is increased to 180°C over night. In this step, a gel is formed and dried. The solid obtained is calcined at 500°C for 4 h and then at 900°C for 12h. The XRD shows the perovskite cubic pattern and the reflection of the CeO_2 phase (Figure 2). The surface area after calcination is 10 m^2/g.

The same CPO material can be obtained by solid state reaction. The precursors chosen are La_2O_3, Fe_2O_3, $Ce_2(CO_3)_3,xH_2O$ and $2NiCO_3,3Ni(OH)_2,4H_2O$. The oxides and carbonates are ball mixed during one hours in alcohol or water. After drying at 50 °C the mixture is calcined at 900 °C during 12 hr. The XRD shows the perovskite cubic pattern and the reflection of the CeO_2 phase (Figure 2). The surface area after calcination is less than 5 m^2/g. The powder could be attrited after calcination to increase the surface area around 8-10 m^2/g.

Example 6

The catalyst of the example 2 was analysed by XRD after reaction and after calcination at 1100°C and reaction (Figure 3). Figure 3 discloses XRD patterns of $La_{0.8}Ce_{0.2}Fe_{0.7}Ni_{0.25}Rh_{0.05}O_3$ catalysts after calcination at 900°C and 1100°C (fresh C9 and C11) before reaction and after CPO tests (used C9 and C11) / (+) ABO_3 perovskite structure, (*) CeO_2 compound. The XRD reported show that the calcined at 1100°C and the reaction does not change the phase composition. In all cases the perovskite structure and a CeO_2 side phase are detected. These analyses confirm the stability of the catalyst at high temperature (> 1000 °C) and in hard reaction conditions. The catalyst does not show the Ni and Rh crystal due to the dispersion of the metals on the catalyst surface.

Results

After reduction of the catalysts under a mixture of N_2 and H_2 at 750 °C / 1 hr, the materials were tested in CPO reactions. The reduction is useful to have immediately the catalyst in its maximum of activity without waiting for stabilisation and to avoid that part

of the catalyst is still oxidised. This activation period (time during which the active phase will be form under reductive conditions) could also be obtained under time on stream with the initial mixture methane/oxygen.

The tests were carried out in a fixed bed quartz microreactor of 8 mm of diameter, loaded with 1.50 g in granules (20-30 mesh). The tests were carried out at atmospheric pressure in three different conditions of feed and two different oven temperature : methane/oxygen/helium 2/1/20 and 2/1/4 v/v at 500°C and 750°C (residence time = 0.2 s) and methane/oxygen/helium 2/1/1 at 750°C (residence time = 0.33 s). The reaction products were analysed by gas chromatography. All the catalyst in all the conditions shows total oxygen conversion. The initial temperature is the temperature of the gas mixture at the beginning of the catalytic bed. The temperature maximal (T_{max}) is the temperature measured at the end of the catalytic bed.

CPO tests of $LaFe_{0.7}Ni_{0.25}Rh_{0.05}O_3$ (Example 1)

The catalyst prepared in the example 1, $LaFe_{0.7}Ni_{0.25}Rh_{0.05}O_3$, is tested under CPO conditions. At low temperature the catalyst behaviour leads to the total combustion products. The methane conversion and the CO and H_2 is high at high temperature (750°C) since the catalyst requires high temperature to be activated.

The test were carried out using methane/oxygen/helium 2/1/20 and 2/1/4 v/v at 500°C and 750°C with residence time of 0.2 s, and methane/oxygen/helium 2/1/1 at 750 °C with a residence time of 0.33 s.

Gas mixture ($CH_4/O_2/He$)	Initial Temperature (°C)	Conv.CH_4 (%)	Sel.CO (%)	Sel.H_2 (%)	T_{max} (°C)
2/1/20	500	27.2	2.5	5	598
2/1/4	500	54.1	58.9	83.9	733
2/1/20	750	92.4	93.2	90.9	802
2/1/4	750	82.2	91.9	92.2	867

CPO tests of $La_{0.8}Ce_{0.2}Fe_{0.7}Ni_{0.25}Rh_{0.05}O_3$ (Example 2)

The catalyst prepared in the example 2, $La_{0.8}Ce_{0.2}Fe_{0.7}Ni_{0.25}Rh_{0.05}O_3$, is tested under CPO conditions. The reaction shows an increase of catalytic activity with respect to the example

1 at low temperature in diluted conditions but is higher also in hard reaction conditions. This is due to the effects of the Ce which promotes the reduction of the catalyst.

The test were carried out using methane/oxygen/helium 2/1/20 and 2/1/4 v/v at 500°C and 750°C with residence time of 0.2 s, and methane/oxygen/helium 2/1/1 at 750°C with a residence time of 0.33 s.

No deactivation of the catalyst is observed after return to initial conditions (500°C, 2/1/20).

Gas mixture ($CH_4/O_2/He$)	Initial Temperature (°C)	Conv.CH_4 (%)	Sel.CO (%)	Sel.H_2 (%)	T_{max} (°C)
2/1/20	500	53.6	30.4	65.8	646
2/1/20	750	93.6	92.9	88	807
2/1/4	750	88	94.4	91.8	880
2/1/1	750	86.9	93.6	91.7	890
2/1/20	*500°C-Ret	55.5	30.8	71.1	640

*500°C ret. is a test carried out at 500°C 2/1/20 to confirm the result of the first test after all the test

CPO tests of $LaFe_{0.7}Ni_{0.3}O_3$ (Example 3, as comparison)

The catalyst prepared in the example 3 $LaFe_{0.7}Ni_{0.3}O_3$. This catalyst shows low activity at low and high temperature due to the not complete reduction of the Ni. The test were carried out using methane/oxygen/helium 2/1/20 and 2/1/4 v/v at 500°C and 750°C with residence time of 0.2 s, and methane/oxygen/helium 2/1/1 at 750°C with a residence time of 0.33 s.

Gas mixture ($CH_4/O_2/He$)	Initial Temperature (°C)	Conv.CH_4 (%)	Sel.CO (%)	Sel.H_2 (%)	T_{max} (°C)
2/1/20	500	26.2	0	0	554
2/1/20	500	32.5	20.1	48	762
2/1/20	750	60.3	71.8	78.8	769
2/1/4	750	64	80.4	91.2	872

CPO tests of $LaFe_{0.95}Rh_{0.05}O_3$ (example 4 as comparison)

The catalyst prepared in the example 4, $LaFe_{0.95}Rh_{0.05}O_3$. The catalyst shows a methane conversion and CO and H_2 selectivities very low in all reaction conditions. This is due to

the fact that the catalyst is not reduced during the activation step in hydrogen flow or in the reaction conditions (methane/oxygen/helium 2/1/20 and 2/1/4 v/v at 500°C and 750°C (residence time = 0.2 s) and methane/oxygen/helium 2/1/1 at 750°C (residence time = 0.33 s).

Gas mixture ($CH_4/O_2/He$)	Initial Temperature (°C)	Conv.CH_4 (%)	Sel.CO (%)	Sel.H_2 (%)	T_{max} (°C)
2/1/20	500°C	27.9	8.3	27.7	578
2/1/20	750°C	36.9	31.2	39.9	827

Aging CPO tests of $La_{0.8}Ce_{0.2}Fe_{0.7}Ni_{0.25}Rh_{0.05}O_3$ (Example 2)

The catalytic results of duration tests of the catalyst prepared as in example 2 ($La_{0.8}Ce_{0.2}Fe_{0.7}Ni_{0.25}Rh_{0.05}O_3$) are reported in figure 4. Figure 4 discloses CPO tests (conversion, selectivity) of $La_{0.8}Ce_{0.2}Fe_{0.7}Ni_{0.25}Rh_{0.05}O_3$ catalyst under time on stream at 500 and 750 °C. The test were carried out using methane/oxygen/helium 2/1/20 and 2/1/4 v/v at 500°C and 750°C with respectively residence time of 0.2 s.

In all cases no deactivation are observed under time on stream. At 750°C the methane conversion is around 90 %, the CO and hydrogen selectivities respectively 94 and 92 %.

The results were compared with those of a commercial catalysts Pt 0.5%wt on alfa Al_2O_3 calcined at 900°C (0.5 % wt Pt/α-Al_2O_3). The results of the duration tests of the commercial catalyst are carried out in the same conditions of the CPO tests of $La_{0.8}Ce_{0.2}Fe_{0.7}Ni_{0.25}Rh_{0.05}O_3$. The comparisons between the two catalysts are described in the next table. The perovskite CPO material presents the same performances and stability as the commercial product.

Gas mixture ($CH_4/O_2/He$)	Initial Temperature (°C)	Time on stream (hr)	Conv.CH_4 (%)	Sel.CO (%)	Sel.H_2 (%)	T_{max} (°C)
Commercial catalyst: Pt (0.5wt%)/α-Al_2O_3						
2/1/20	500°C	1	44.7	31.2	76.5	614
2/1/20	500°C	40	37.7	24.2	65.8	620
2/1/4	750°C	1	91.2	96.6	92.6	842
2/1/4	750°C	40	87.7	95.7	93.4	935
Perovskite catalyst : $La_{0.8}Ce_{0.2}Fe_{0.7}Ni_{0.25}Rh_{0.05}O_3$						
2/1/20	500	1	53.6	30.4	65.8	646
2/1/20	500	40	56.0	31.0	67.0	650
2/1/4	750	1	88	94.4	91.8	880
2/1/4	750	40	86.9	93.6	91.7	890

The advantages of the perovskite catalysts are the thermal stability in hard reaction conditions the high activity at short residence time and the presence of synergetic effect among Rh and Ni.

CLAIMS

1. Composition characterized in that it essentially consists in a solid solution of a mixture of at least a perovskite cristallographic structure with nickel and/or rhodium metal.

2. Composition according to claim 1, represented by the general formula (I) :

$$[A_zA'_{1-z}][B_{1-x-y}Ni_x Rh_y]O_{3-\delta} \qquad (I)$$

wherein :

A and A' are different and are selected from the Lanthanide or the Actinide families or from the group II_a of the Mendeleev's periodical table of elements;

B is selected from the transition metal groups of columns IIIb, IVb, Vb, VIb, VIIb, Ib and IIb and group VIIIb of the Mendeleev's periodical table of elements;

$0 < x \leq 0.7$,

$0 < y \leq 0.5$,

$0 \leq x+y \leq 0.8$,

$0 \leq z \leq 1$ and

δ is the sub stœchiometric value of oxygen to obtain the electric neutrality of the Perovskite compound.

3. Composition according to claim 2, wherein A and A' are independently chosen from La, Ce, Ca or Sr.

4. Composition according to claim 3, wherein A is La.

5. Composition according to claims 1 to 4, wherein B is chosen from Mn, Fe, Co or Al.

6. Composition according to claim 2, represented by the formula (Ia):

$$[La_zA'_{1-z}][Fe_{1-x-y}Ni_x Rh_y]O_{3-\delta} \qquad (Ia)$$

wherein A', x, y, and z and δ are as hereinabove defined for the formula (I).

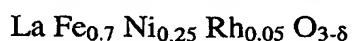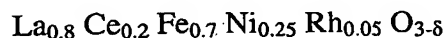7. Composition according to claim 6, represented by the formula (Ib) :

$$[La_zCe_{1-z}][Fe_{1-x-y}Ni_x Rh_y]O_{3-\delta} \qquad (Ib)$$

wherein x, y, and z and δ are as herein above defined for the formula (I),

8. Composition according to claims 2 to 7, wherein $0 < x \leq 0.5$.

9. Composition according to claims 2 to 8, wherein, $0 < y \leq 0.25$, and z < 1.

10. The following compositions :

$$La Fe_{0.7} Ni_{0.25} Rh_{0.05} O_{3-\delta}$$

$$La_{0.8} \, Ce_{0.2} \, Fe_{0.7} \, Ni_{0.25} \, Rh_{0.05} \, O_{3-\delta}$$

$$La_{0.8} \, Ce_{0.2} \, Fe_{0.7} \, Ni_{0.3} \, O_{3-\delta}$$

11. Use of a composition according to any claim 1 to 10 which the operating catalyst conditions are in the range of 500 to 1300 °C and preferably between 600 to 1100°C,

12. Use of a composition according to any claim 1 to 10 which the operating catalyst conditions are in the range of 10^5 Pa to $3 \cdot 10^6$ Pa and preferably between 10^5 Pa to 10^6 Pa.

13. Use of a composition according to any claim 1 to 10 which the operating catalyst conditions are any oxydant feed, preferably pure oxygen, oxygen and inert gas mixture, steam, carbon dioxide or a mixture of part or/and all of them.

14. Use of a composition according to claims 1 to 10, as a catalyst of the partial oxydation of natural gas and/or light hydrocarbons to synthesis gas, as a catalyst of the steam and/or dry reforming of natural gas and/or light hydrocarbons (C1-C4) to synthesis gas or as a catalyst of selective oxidations, as a catalyst of hydrogenation reactions or as a catalyst of dehydrogenated oxydative reactions.

ABSTRACT

The present patent deals with new catalysts for the Catalytic Partial Oxidation (CPO) of methane to synthesis gas (hydrogen and carbon monoxide), a gas mixture widely employed in industry. The discovered perovskite catalysts allows to carried out the process at low residence time obtaining a long time stability in the reaction conditions notwithstanding the high temperature reached in the reactor. The fundamental component of the catalyst is the perovskite structure $[A_zA'_{1-z}][B_{1-x-y}Ni_x Rh_y]O_{3-\delta}$ obtained using mainly La, Sr, as A and A' cation sites (A, A': actinide and/or lanthanide, elements and/or elements from Group I and II) and mainly Fe, Ni, as B cation sites (B : transition metal element and/or element from Group III to V). The active phases Ni and/or Rh are inserted in the perovskite structure during the preparation and are reduced in situ or before the catalytic tests. The insertion of the Rh and Ni in the perovskite structure allows an high dispersion of the metal on the surface and increases its interaction with the perovskite matrix ensuring high activity and stability. The presence of both Rh and Ni is necessary to reach high catalytic performances since the reducibility and the stability in the reduced state is affected by the contemporary presence of the cations. The choice of the A, A' elements are critical for the initial performances and the stability under time on stream of the catalyst for CPO reaction. The element are chosen in order of preference in the lanthanide family (La, Ce, ...) and the Group II.
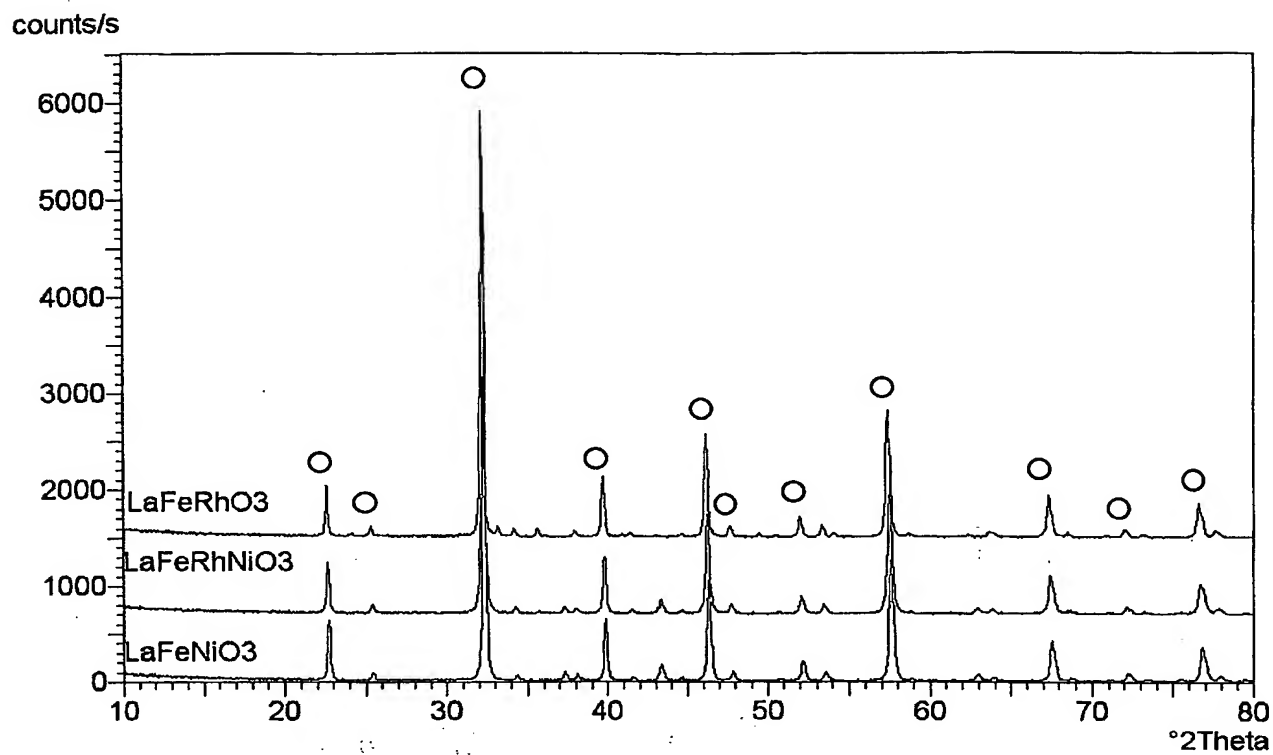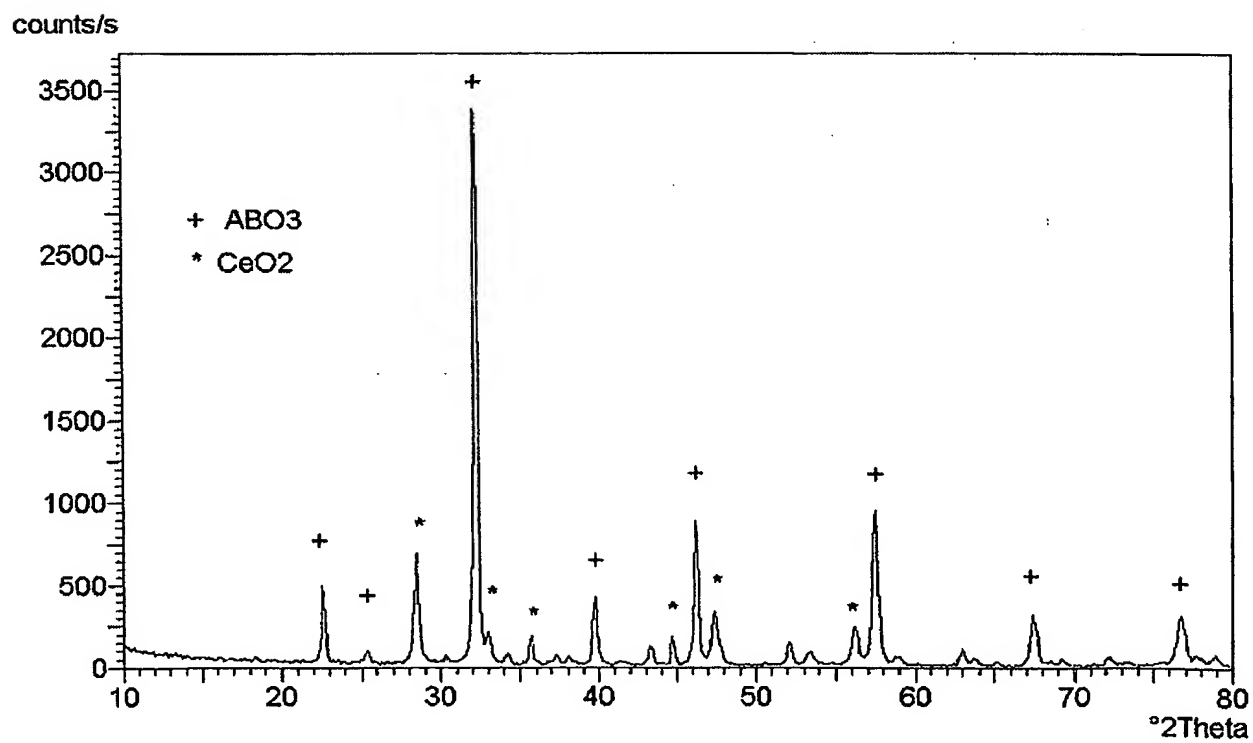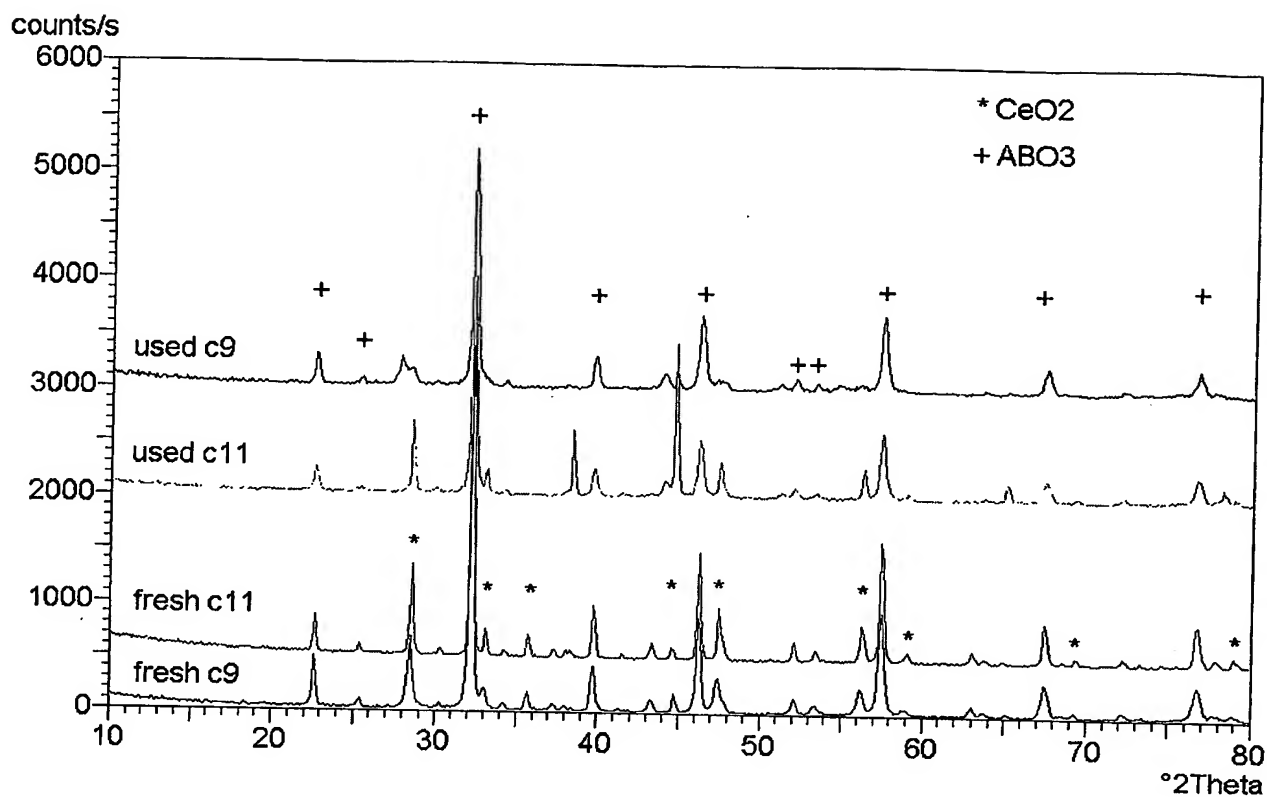
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FIG. 1

counts/s

LaFeRhO3

LaFeRhNiO3

LaFeNiO3

°2Theta

FIG. 2

counts/s

+ ABO3
* CeO2

°2Theta

FIG. 3

FIG. 4